

Growth of Multi-Walled Carbon Nanotubes by Injection CVD Using Cyclopentadienyliron Dicarbonyl Dimer and Cyclooctatetraene Iron Tricarbonyl

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Keywords

Carbon nanotubes, chemical vapor deposition, catalyst, TGA, Raman

Abstract

Preferential oriented multiwalled carbon nanotubes were prepared by the injection chemical vapor deposition (CVD) method using either cyclopentadienyliron dicarbonyl dimer or cyclooctatetraene iron tricarbonyl as the iron catalyst source. The catalyst precursors were dissolved in toluene as the carrier solvent for the injections. The concentration of the catalyst was found to influence both the growth (i.e., MWNT orientation) of the nanotubes, as well as the amount of iron in the deposited material. As deposited, the multiwalled carbon nanotubes contained as little as 2.8% iron by weight. The material was deposited onto tantalum foil and fused silica substrates. The nanotubes were characterized by scanning electron microscopy, transmission electron microscopy, Raman spectroscopy and thermogravimetric analysis. This synthetic route provides a simple and scalable method to deposit MWNTs with a low defect density, low metal content and a preferred orientation.

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Introduction

The area of carbon nanotubes has developed rapidly during the past decade since their discovery [1]. Nanotubes and nanofibers have been produced by several techniques including arc discharge [1,2], laser ablation [3], flame synthesis [4] and a variety of chemical vapor deposition (CVD) methods [5-9]. Two of the most promising methods for depositing commercial quantities of aligned multiwalled carbon nanotubes are the “floating catalyst” CVD method [10-13] and the injection CVD method [14-22]. For the injection method, an organic solvent containing a dissolved organometallic compound that decomposes to form the catalysts is injected into a two-zone furnace. In the first zone, both the solvent and the catalyst vaporize. A carrier gas sweeps the vapors into the second zone where the organometallic compound decomposes to yield nanoparticles of the metal catalyst. Solvent and ligand molecules serve as the carbon source for nanotube growth at the catalyst sites. The organometallic compounds commonly used are metallocenes (Fe, Co, Ni or Ru) [15-22] and iron pentacarbonyl, $[\text{Fe}(\text{CO})_5]$ [23,24]. Our work has sought to explore a wider range of organometallic catalyst precursor compounds in an effort to realize a more efficient carbon nanotube synthesis route. Here we present multiwalled carbon nanotube growth using cyclopentadienyliron dicarbonyl dimer and cyclooctatetraene iron tricarbonyl as the iron catalyst source. The photochemistry of cyclopentadienyliron dicarbonyl dimer was extensively studied nearly two decades ago [25], but this is the first report of either compounds use for carbon nanotube growth.

Experimental

All operations of moisture- and air-sensitive materials were performed under an argon atmosphere employing standard Schlenk techniques and a double-manifold vacuum line. Solids were manipulated in an argon filled glovebox. Solvents were freshly distilled from appropriate

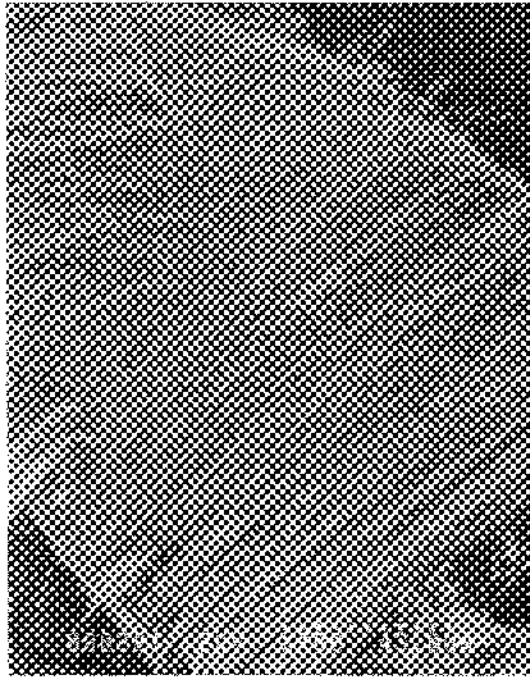
drying agents under argon prior to use. The organometallic catalyst precursors cyclopentadienyliron dicarbonyl dimer (Sigma-Aldrich Chemical Company) and cyclooctatetraene iron tricarbonyl (Strem Chemical Company) were used as received.

Multiwalled carbon nanotubes were deposited using a modified version of our atmospheric pressure aerosol assisted CVD reactor [26-31]. Toluene solutions of the catalyst precursor (0.06 M cyclopentadienyliron dicarbonyl dimer or 0.20 M cyclooctatetraene iron tricarbonyl) were injected through a 20 gauge needle into the first zone of a two zone furnace using a syringe pump. Solutions were injected at rates ranging from 1.5 - 2.0 ml/hr, with typically 2.5 - 4 ml being delivered. The temperature of zone one was held at $200 \pm 1^\circ\text{C}$, which is above the boiling point of the solvent and above the decomposition temperature of the precursors. A mixed carrier gas of 4% hydrogen in nitrogen or argon (1.5 slpm) swept the hydrocarbon and catalyst gases into the hot zone of the furnace. Multiwalled carbon nanotubes were deposited onto tantalum foil and SiO_2 substrates as well as onto the walls of the 35 mm fused silica reactor tube in the hot zone. The material was either characterized directly on the substrates or retrieved from the walls of the tube and subsequently characterized. The as-synthesized materials were characterized by scanning electron microscopy (SEM) (Hitachi S-3000N), field emission SEM (Hitachi S-900), Raman spectroscopy (J-Y Horiba), and thermogravimetric analysis (TGA) (TA Instruments TGA 2950). Nanotubes ultrasonically dispersed in methanol were characterized by high resolution transmission electron microscopy (HRTEM) with Energy Dispersive Spectroscopy (TEM-EDS) (Philips CM 200).

Results and Discussion

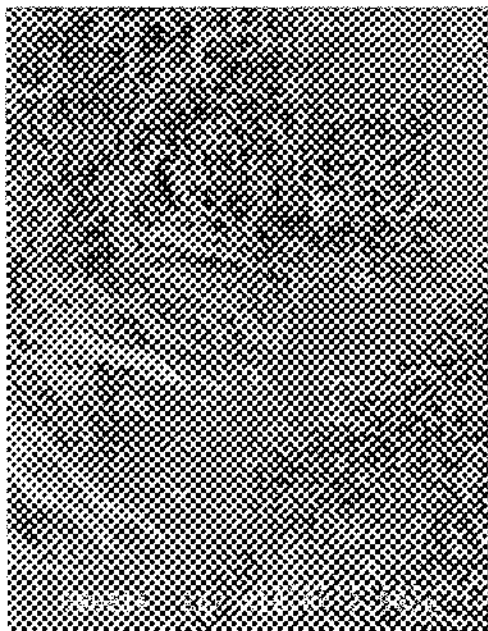
Aligned multiwalled carbon nanotubes were prepared using either cyclopentadienyliron dicarbonyl dimer or cyclooctatetraene iron tricarbonyl as iron catalyst sources. The material coated the Ta foil and SiO₂ substrates, as well as the quartz reactor tube. The tube was coated from just inside the hot zone of the furnace and extending back inside the furnace 100 mm, with the surface temperature ranging from 685-750°C, as measured by a thermocouple. The as-synthesized material, which was easily removed from the surface of the quartz tube, resembled charred paper. Samples were coarse, fibrous materials that when imaged by SEM displayed a preferential degree of alignment in cross-section, with the growth axis normal to the growth surface (Figure 1). The outside diameter of the nanotubes ranged from 15 – 200 nm (estimated from the TEM and SEM results), which is consistent with results others have obtained using metallocenes and injection CVD [17,19,32]. Since it has been widely reported that the nanotube diameter varies directly with the concentration of metal catalyst in solution and in the gas phase [19,22], attempts were made to prepare smaller diameter nanotubes using lower metal concentrations. Growth was attempted using a cyclopentadienyliron dicarbonyl dimer concentration of half of the original concentration (0.03 M). Growth conditions using the lower concentration were not as optimized as with the higher concentration. Instead of depositing in a limited region of the quartz tube as with the higher concentration, a fine powder coated the entire length of the tube in the hot zone. However, the lower metal concentration was effective at reducing the overall size distributing of the nanotubes, with the size determined from electron microscopy ranging from 15-70 nm. Nanotube growth under these conditions was more random and less aligned than with the more concentrated solutions (Figure 2). These results are consistent with what others have observed when catalyst concentrations are too low for optimal deposition [22].

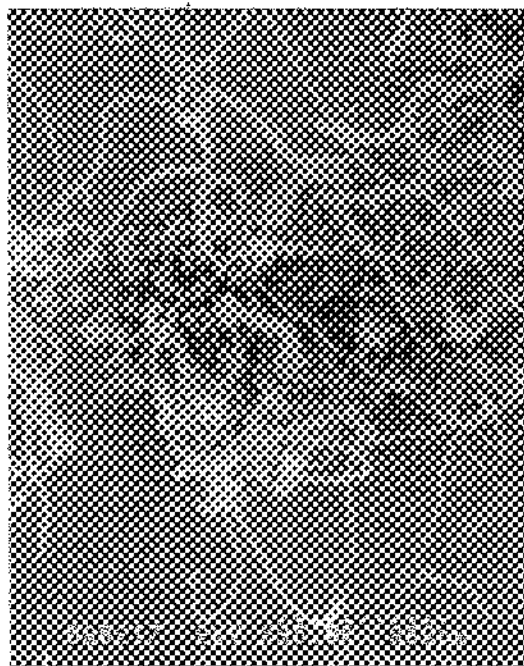
[Figures 1 and 2 here]



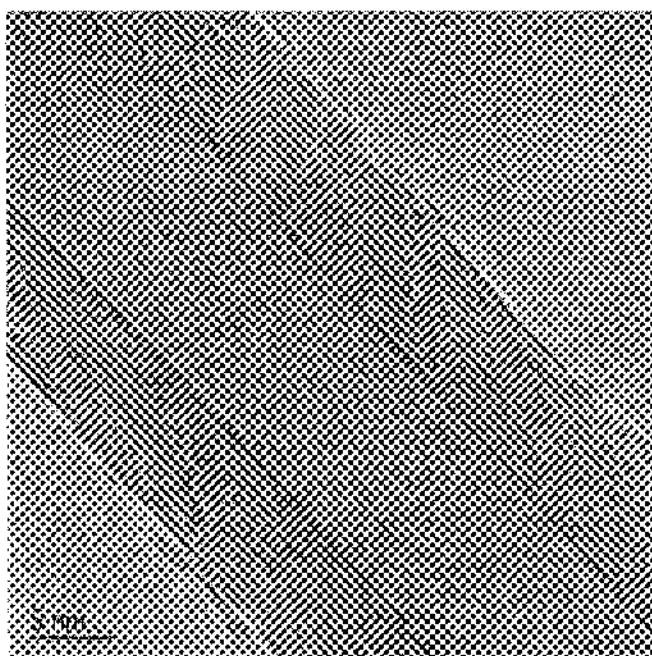
Using cyclooctatetraene iron tricarbonyl, multiwalled nanotubes were grown onto Ta foil and SiO₂ substrates. Depositions onto the tantalum foil yielded less complete surface coverage than depositions onto SiO₂ surfaces (figure 3). An interesting feature that appears in materials deposited onto the metal foil is a randomly oriented, fibrous growth on the metal surface (figure 4). Presently, the nature of the material is unknown, but in the SEM it appears to be graphitic carbon fibers. The nanotubes grow off of this material. As evidenced by the SEM, nanotube growth on the Ta foil was also less ordered than growth on the quartz, which is likely the result of growing from the randomly oriented fibers instead of from a smooth surface. Estimated from SEM results, the outside diameter of the nanotubes grown on the Ta foil typically ranged from 22 – 76 nm, with a few as small as 7.0 nm. Diameters for the fibrous material on the surface ranged up to 82 nm.

[Figure 3 and 4 here]





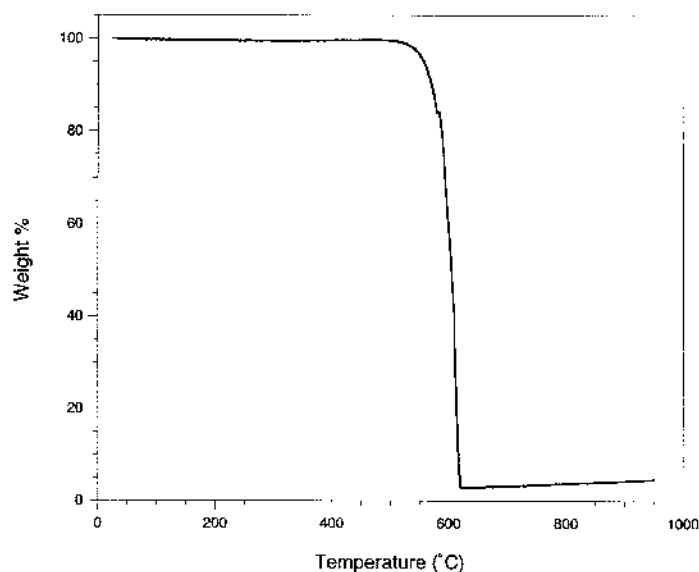
High resolution transmission electron microscopy characterization of nanotubes grown using cyclopentadienyliron dicarbonyl dimer revealed multiwalled nanotubes with a wide range in inner diameters, in addition to the outer diameter range. Inner diameters were found to range from 2.6 – 31.6 nm (Figure 5). Most of the tubes were hollow, but some contained nanorods of iron (as determined by TEM-EDS) with lengths up to 150 nm and iron nanoparticles with diameters ranging from 14.0-34.0 nm. The smallest carbon nanotubes observed had six concentric walls with the normal 0.34 nm spacing.



[Figures 5 here]

Multiwalled carbon nanotubes grown using both iron catalyst sources were additionally characterized by thermogravimetric analysis in air (Figure 6). Carbon nanotubes prepared using the higher concentration of cyclopentadienyliron dicarbonyl dimer had minimal weight loss below 520°C, losing only one percent of its mass by 522°C. The maximum weight loss per degree occurred at 609°C, and all carbon was converted to CO₂ by 625°C. The residue after complete carbon oxidation was 2.8 wt. % of the original mass and was found to be iron by dissolving the residue in an HCl solution to yield a red solution, indicative of iron. As prepared, the metal concentration in the synthesized material is considerably lower than others have reported using metallocenes or iron pentacarbonyl, where residual iron commonly ranges from 7-22 wt. % [7,33].

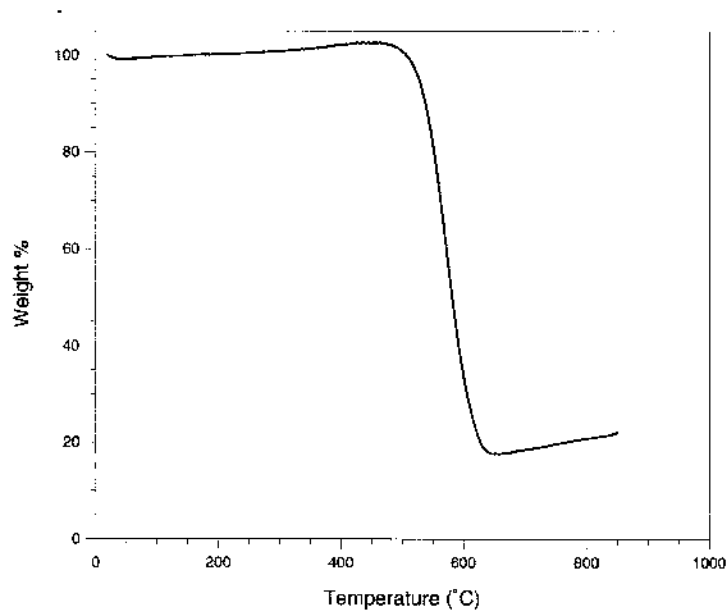
[Figures 6 here]



Although lower catalyst concentrations of cyclopentadienyliron dicarbonyl dimer were effective at reducing the overall size distribution of the nanotubes, surprisingly these materials also yielded higher levels of iron. As characterized by TGA, the iron content actually increased to 17.6 wt. %, for the nanotubes prepared using the more dilute injection solution.

Thermogravimetric analysis shows a modest increase in weight with temperature increase that peaks at 102.6 wt. % at 444°C (Figure 7), which is likely caused from oxidation of iron particles on the surface of the nanotubes. Maximum weight loss occurred at 573°C, with all of the carbon being oxidized by 650°C. The higher iron content further demonstrates the non-optimal growth conditions of the diluted solution.

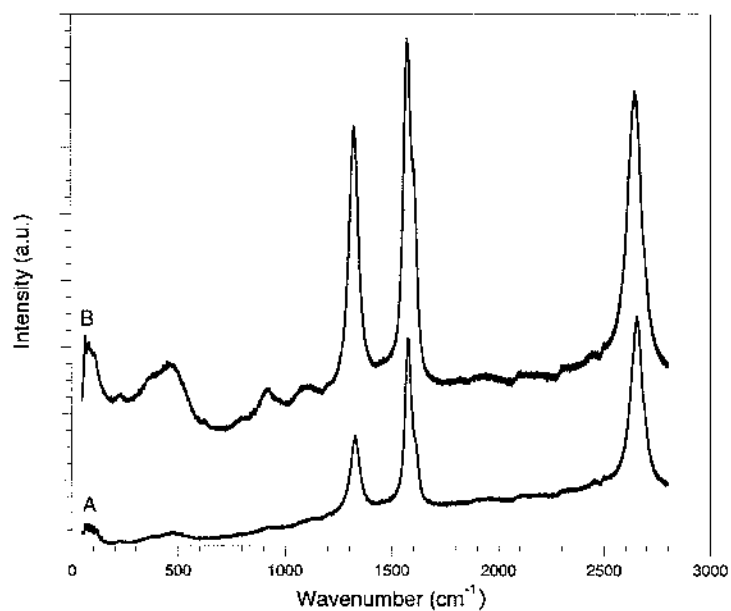
[Figures 7 here]



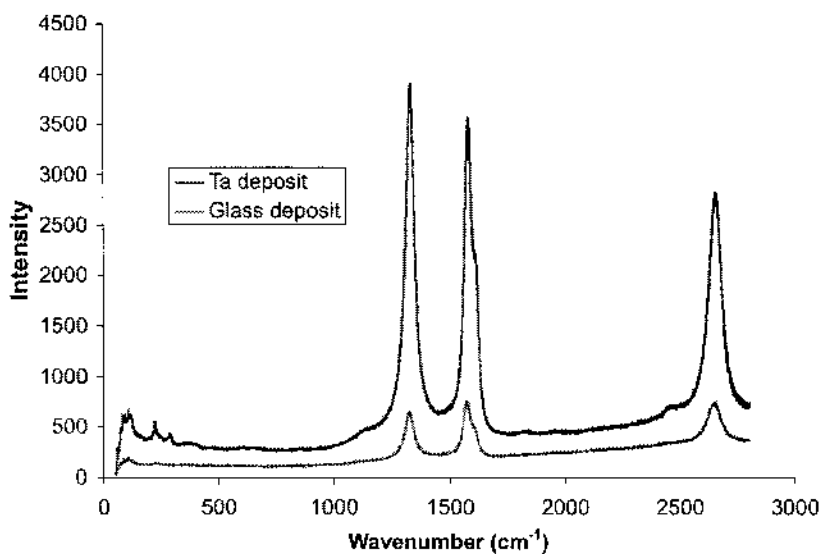
Carbon nanotubes deposited using both concentrated and dilute solutions of cyclopentadienyliron dicarbonyl dimer as the catalyst source were also characterized by Raman spectroscopy (Figure 8.a. and 8.b.). The Raman spectrum for multiwalled carbon nanotubes deposited using higher concentrations reveal strong bands at 1331 cm^{-1} , 1581 cm^{-1} and 2659 cm^{-1} , corresponding to the D, G, and D* lines, respectively, with the shoulder at 1616 cm^{-1} corresponding to the D' line [34]. These lines shift slightly in samples prepared using the less concentrated solution but are well within the range of what others have measured [16,35]. The G band has E_{2g} symmetry and arises from in-plane bond stretching of pairs of sp^2 carbon atoms. The D band is a symmetrical stretch with A_{1g} symmetry. It is forbidden in perfect graphite, but becomes active as disorder increases [36]. The ratio of the intensity of the D and G bands (I_D/I_G) is often used as a measure of disorder in carbon nanotubes [22,37]. As evident from the Raman spectra, there is more disorder in the material prepared with the lower catalyst concentration than in that prepared with the higher cyclopentadienyliron dicarbonyl dimer concentration, where the

I_D/I_G ratio for as-prepared nanotubes are 0.47 and 0.76 for the material prepared using higher and lower iron catalyst concentration, respectively. This is likely a result of the conditions yielding a cleaner, more controlled deposition with the more concentrated solution. The D^* mode in the Raman spectrum gives a sharp line at 2659 cm^{-1} and is the overtone of the D line (i.e., $\sim 2 \times 1331\text{ cm}^{-1}$).

The Raman spectrum was also measured for the material grown onto Ta foil and SiO_2 substrates using cyclooctatetraene iron tricarbonyl (Figure 9). The I_D/I_G ratio for as-deposited material, measured directly on the Ta and SiO_2 surfaces are 1.11 and 0.86, respectively. Both ratios are larger than the I_D/I_G ratio for nanotubes grown using cyclopentadienyliron dicarbonyl dimer, with the ratio for the tubes on Ta foil being the largest. The authors speculate that the increased disorder in the material grown on tantalum, as evident from the Raman spectrum is a product of both nanotube growth on top of the fibrous graphitic material, and the Raman spectrum containing data from both the surface material and the nanotubes. The small peaks around 250 cm^{-1} and below in all spectra could arguably be assigned to single walled carbon nanotubes, but no evidence of their presence was found by HRTEM. If any of the material does contain single walled nanotubes, they are likely only a small fraction of the sample.



[Figures 8 + 9 here]



Conclusion

Aligned, multiwalled carbon nanotubes were grown by injection CVD using either solutions of cyclopentadienyliron dicarbonyl dimer or cyclooctatetraene iron tricarbonyl

dissolved toluene. The material was deposited onto Ta foil and SiO₂ substrates and the walls of a fused silica tube. Using 0.06 M solutions of cyclopentadienyliron dicarbonyl dimer, as grown nanotubes contained less than 3% iron by weight. Ironically, when less concentrated solutions were used, the amount of iron in the material increased, and nanotube growth was less controlled and less ordered. Nanotube growth onto Ta foil substrates yielded less uniform growth than that obtained on SiO₂ surfaces. If growth onto conductive substrates can be optimized to dense, uniform films, then this technique could be used to produce carbon nanotube-based anodes for lithium-ion batteries.

Acknowledgment

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Figure Captions:

Figure 1. Cross-sectional view of carbon multiwalled carbon nanotubes grown using cyclopentadienyliron dicarbonyl dimer as the iron source.

Figure 2. Carbon nanotubes grown using a low concentration of cyclopentadienyliron dicarbonyl dimer.

Figure 3. SEM image of carbon nanotubes grown on a tantalum substrate. Note incomplete surface coverage.

Figure 4. SEM image of fibrous graphitic material on the tantalum surface.

Figure 5. TEM image of a multiwalled carbon nanotube grown using cyclopentadienyliron dicarbonyl dimer as the iron source.

Figure 6. TGA of carbon nanotubes grown using cyclopentadienyliron dicarbonyl dimer as the iron source.

Figure 7. TGA of carbon nanotubes grown using a low concentration of cyclopentadienyliron dicarbonyl dimer.

Figure 8. Raman spectra of carbon nanotubes grown using (A) normal concentration and (B) low concentrations of cyclopentadienyliron dicarbonyl dimer.

Figure 9. Raman spectra of carbon nanotubes grown on tantalum (upper) and fused silica (lower) substrates using cyclooctatetraene iron tricarbonyl.